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1967 CONFERENCE ON CITRUS CHEMISTRY AND UTILIZATION

OCTOBER 13, 1967

ABSTRACTS OF PAPERS

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AGRICULTURAL RESEARCH SERVICE

UNITED STATES DEPARTMENT OF AGRICULTURE

PROGRAM

1967 CONFERENCE ON CITRUS CHEMISTRY AND UTILIZATION

October 13, 1967

ANALYSES OF STORED FOAM-MAT ORANGE AND GRAPEFRUIT CRYSTALS AND OF MODEL SYSTEMS

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(Presented by M. K. Veldhuis)

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FLAVOR EXTRACTION WITH LIQUID CO_2

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(Presented by R. Larry Merson)

JUICE CONCENTRATION BY REVERSE OSMOSIS

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ANALYSES OF STORED FOAM-MAT ORANGE AND GRAPEFRUIT CRYSTALS AND OF MODEL SYSTEMS

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Foam-mat dried orange and grapefruit crystals undergo nonenzymic browning upon prolonged storage at elevated temperatures. Generally, when stored under identical conditions, orange is first to develop a detectable flavor change. Orange and grapefruit were analyzed when a flavor change could first be detected by an experienced taste panel. In both samples, the same storage products were present in about the same quantities.

In studies of isolation of nonenzymic products formed during storage, 18 compounds have been identified thus far. Table I lists these as well as the compound believed from model studies to be the precursor for some of these storage products.

In addition to the fructose-acid model system reported on at last year's Citrus Conference, both a fructose-base model system and an ascorbic acid model system have been studied for further insight into the source and mechanisms of formation of storage products. Of special interest from the fructose-base degradation model system was the presence in the product mixture of compound 18 (Table I). This substance is a flavor component of pineapple concentrate and it has a sweet caramel-like odor.

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A PROCEDURE FOR OBTAINING RADIOACTIVE NARINGIN FROM GRAPEFRUIT LEAVES FED L-PHENYLALANINE-^{14}C

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(To be presented by M. K. Veldhuis)

In recent years progress has been made in debittering grapefruit by removing the most prevalent bitter constituent naringin from the commercial product by various means. A different approach to the problem is to prevent the bitter constituents from being biosynthesized in the plant. To this end an investigation was undertaken to study the biogenesis of naringin and its tasteless isomer naringenin-7β-rutinoside.

The use of radioisotopes to label a compound allows one to follow a certain compound in its normal metabolic pathways in a living system and thus offer a possible clue as to where one can disrupt this normal biogeneric pathway and prevent the synthesis of the compound in question. To this end attempts were made to find a precurser to the biosynthesis of naringin. C^{14}-carbon dioxide was readily photosynthesized into naringin. However, since incorporation of CO_2 is so general in the plant system, CO_2 did not readily offer us a tool in understanding the biogeneric pathway of naringin. Phenylalanine has been reported to be a precurser to flavonoids in buckwheat and since biogeneric pathways generally are not specific to one species, phenylalanine was a most likely candidate as a precurser to the flavonoid naringin. When young grapefruit leaves were fed L-phenylalanine^{14}-C, radioactive naringin (Naringenin-7β-neohesperidoside) and naringenin-7β-rutinoside were isolated.

The method employes radiolabeled L-phenylalanine which is taken up by young grapefruit leaves through the petioles. The leaves are then allowed to metabolize the phenylalanine during periods of twelve hours of light and twelve hours of dark. Extraction of the leaves with hot methyl alcohol, followed by concentration and column chromatography afforded both the bitter naringin and its tasteless isomer. Final separation and purification of both compounds were accomplished by thin-layer chromatography. The availability of these radiolabeled compounds will enable us to advance our knowledge concerning the site of synthesis and translocation of naringin as well as its biosynthesis and metabolism in the grapefruit plant. The availability of radiolabeled naringin allows chemists to synthesize labeled derivatives of naringin such as the dihydrochalcone, a possible sugar substitute, for further tracer research. Another possible use for these compounds is in analytical methods for naringin in which a certain amount of the labeled naringin would be added to a sample, mixed and a small amount of pure naringin recovered. From the radioactivity of the sample recovered and the amount of radioactive naringin added, the amount of original naringin could be calculated. This procedure would be applicable to very small samples.

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BASIC STUDIES ON ENZYMES IN CITRUS PRODUCTS

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The purpose of these studies was to determine whether or not mature citrus fruit is capable of supporting the types of oxidation reduction reactions that are associated with biosynthetic processes in plant tissue. This information is essential to our recently initiated Enzyme Research Program in developing an experimental approach to select and study those reactions in the biosynthetic pathway of aliphatic and terpenoid oxygenated compounds that can be controlled during processing of citrus so as to enhance the flavor of fruit and juice products.

The type reaction under investigation requires the coenzyme, nicotinamide adenine dinucleotide (NAD), or its phosphate (NADP). This type of reaction accounts for most of the known oxidations and reductions that occur in the various reaction pathways of plant tissue metabolism. The coenzyme functions as the electron acceptor during the oxidation of a compound as in the degradative pathway of fatty acid (Figure 1a) and as the donor in the reduction reaction as in the biosynthetic pathway to the terpenoids (Figure 1b).

The coenzyme is loosely bound to the enzyme so that the same coenzyme molecule can serve first as a reductant for one reaction and then as an oxidant for a second reaction. This versatility enables the coenzyme to function as an effective regulator of a series of metabolic reactions.

We examined extracts of juice sacs from mature oranges and grapefruit to determine the distribution of the coenzymes in their reduced and oxidized forms.

The results of our analyses are shown in Table I. NADP was present mostly as the reduced form, whereas the oxidized form of NAD was predominant in both fruits.

Assuming that all of the NADP is available for enzyme reactions, then these results indicate that more than one-half is available for the reductase reactions and suggest that in terms of coenzyme requirements conditions in mature fruit are favorable for biosynthesis.

The low ratio of reduced to oxidized NAD suggests that mature fruit has a very active oxidase for $NADH_2$. Four terminal oxidases and corresponding coupling reductases that oxidize $NADH_2$ are known to occur in plant tissue. These are listed in Figure 2. Since one or more of these systems might be the responsible oxidant, we examined particulate fractions from juice sacs of mature grapefruit and oranges for oxidase activity with $NADH_2$, cytochrome c, ascorbate, catechol, and glycollate.

Cytochrome c was the only substrate that was rapidly oxidized, although some activity was detected with ascorbate and catechol. Highest activity was observed in the particulate fraction that sedimented between 1000 and 10,000 x G in 15 minutes. This fraction from the orange oxidized cytochrome c in terms of oxygen consumed at the rate of 14 microatoms of O_2 per hour per mg of protein in the fraction. The corresponding fraction from grapefruit was only about one-third as active.

The fraction with the highest cytochrome c oxidase activity also had the highest $NADH_2$-cytochrome c reductase activity. Expressed in terms of O_2 utilized, the rate of oxidation by the reductase was 5 microatoms of O_2 per hour per mg protein. The coupling of the reductase and the oxidase through cytochrome c to form an $NADH_2$-oxidase is diagramed in Figure 2.

These observations on the oxidation of $NADH_2$ indicate that mature grapefruit and oranges have an active NAD oxidase system and suggest that coupling the oxidation of $NADH_2$ through cytochrome c reductase to molecular O_2 probably serves as the energy generating system for biosynthetic reactions in citrus.

FIGURE 1

TYPICAL REACTIONS REQUIRING NAD AND NADP

a.

$$\text{R-CHOH-CH}_2\text{-CO-CoA + NAD} \xrightarrow{\text{3-hydroxyacyl-CoA dehydrogenase}} \text{R-CO-CH}_2\text{-CO-CoA + NADH}_2$$

b.

$$\text{COOH-CH}_2\text{-C(OH)(CH}_3\text{)-CH}_2\text{-CO-CoA + 2NADPH}_2 \xrightarrow{\text{Hydroxymethylglutaryl-CoA reductase}} \text{COOH-CH}_2\text{-C(OH)(CH}_3\text{)-CH}_2\text{-CH}_2\text{OH + CoA + 2NADP}$$

CoA stands for Coenzyme A: 3'phospho-adenosine diphosphate-pantoyl-β-alanyl-cysteamine.

FIGURE 2

COUPLING OF $NADH_2$ OXIDATION TO TERMINAL OXIDASE

Terminal Oxidase	Coupling Reductase
cytochrome c oxidase	cytochrome c reductase
ascorbic acid oxidase	dehydroascorbic acid and glutathione reductase
phenol oxidase	quinone reductase
glycollic acid oxidase	glyoxylic acid reductase

$DPNH_2$

$DPNH_2$ cytochrome c reductase

DPN

ferro cytochrome c

ferri cytochrome c

cytochrome c oxidase

H_2O

1/2 O_2

TABLE I

CONCENTRATION OF PYRIDINE NUCLEOTIDE COENZYMES IN JUICE SACS FROM MATURE ORANGES AND GRAPEFRUIT

	$NADPH_2$	NADP	$\frac{NADPH_2}{NADP}$	$NADH_2$	NAD	$\frac{NADH_2}{NAD}$
Grapefruit	0.92	0.69	1.3	0.51	3.95	0.13
Oranges	1.22	0.93	1.3	1.65	7.86	0.21

Each value represents concentration in micrograms per ml juice and is the average of 10 samples.

CHEMICAL CHARACTERIZATION OF LEMON JUICE PRODUCTS

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A large percentage of the U. S. Lemon crop is processed into juice and juice products. These products are sold commercially on the basis of their acidity which is primarily citric acid. It is sometimes desirable to be abl to characterize lemon juice in terms of constituents other than citric acid. In an attempt to achieve this goal, methods of analysis were adapted to lemo juice for the measurement of total acidity as citric acid, total amino acids by formol titration, l-malic acid by optical rotation, and total phenolics b UV absorbance. Originally, 61 samples of California and Arizona lemon juic concentrates were analyzed for these constituents. The data were treated b a multiple regression approach. This yielded an equation wereby the citric acid content of a sample could be predicted on the basis of these other constituents. Confidence limits were set at the 99% level which gave a maximum citric acid difference of 19.1 meq/100 ml. This means that with natural juice, titrated citric acid values will be no more than 19.1 units away from the predicted values in 99 cases out of 100.

To further characterize lemon juice the individual amino acids were chromatographed on paper and passed through a recording densitometer. The pattern was fairly constant. Individual phenolics were also estimated by a paper chromatographic system and densitometer. The sum of the individual compounds closely followed the UV absorbance.

A method for the extraction and measurement of sterols and carotenoids was developed, and many lemon juice samples were tested. Correlation studie

of the carotenoid and sterol values with the other constituents used in the multiple regression showed no significant improvement in the reliability of the equation with the additional analyses.

A study of the effects of fruit storage on the selected constituents showed that in one batch of lemons the l-malic acid dropped 64% in 15 weeks. The amino acid concentration increased by 34%, while the total phenolics and citric acid remained constant. In spite of these changes the citric acid value predicted by the multiple regression equation remained nearly constant.

The use of heavy extraction pressures by an FMC extractor, as compared wi light pressures, produced a small increase in the total amino acids and total phenolics in the extracted lemon juice. The other constituents were unchanged Tighter juice finishing pressures had the effect of increasing the pectin content but not the other constituents. The relationship between the predicted and measured citric acid values was not greatly changed.

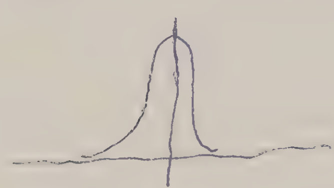
Bottled lemon juice intended for room temperature storage at the retail level is commonly treated with chemical preservatives to prevent deterioration. A study of the effects of sulfur dioxide, sodium benzoate, and potassium sorbat preservatives on the previously mentioned analytical methods confirmed that there is no initial effect caused by these preservatives (except for the formo determination of amino acids, in which case the added SO_2 had to be expelled b boiling 1 min.). On storage of the preserved juices at 5-35°C for up to 17 weeks, small but statistically significant changes in composition were observe in some of the juice samples. For practical applications the changes did not affect the multiple regression approach.

There are a number of other factors which could conceivably influence the composition of the juice such as variety, season, growing area, and cultural

practices which have not yet been thoroughly investigated in this study. Furthermore, it would be impractical to even consider the many possible combinations of factors. However, the limited investigations into some of the important ones indicate that the multiple regression approach may be applied to chemically characterize any commercial lemon juice product.

Regression formula

CA = 36.54 + 12.014 A + 2.71 MA + 3.06 TP



WHAT IS A NATURAL FLAVOR

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Flavors come in various types and sizes. A few occur just as we savor them; citrus fruits are of this type. Others are produced enzymically when tissue is damaged, onions and garlic are the classical examples. Some are produced by fermentation. Processing steps produce flavors, ham and corned beef illustrate these. Most of our foods derive their essential flavor from chemical reactions that occur during cooking. We have herbs and seasonings, monosodium glutamate and now nucleotides. Which of these are natural flavors?

$R-\overset{O}{\overset{\|}{S}}-S-R + H_2O$ alliinase

Onion flavor

R may be CH_3 C_3H_7 or C_3H_5

Propanil is responsible for fresh onion + garlic pungency, bitterness, lachrimation, odor etc.

Enzyme, added to cooked tomato, restores fresh flavor

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POTENTIAL UTILIZATION OF SOME CHEMICALS FROM CITRUS FRUIT

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A number of potential new chemical byproducts from citrus have been proposed recently by members of the staff of the Fruit and Vegetable Products Laboratory. This paper will summarize these proposals with comments on the potential economic return to be expected. In some cases, the chemical reactions involved are somewhat speculative. However, the intent of this paper is only to suggest promising chemical routes to new products.

PEEL OIL:

d-Limonene, the major constituent of citrus peel oils is currently available in 10 to 20 million pound quantities annually at 10 to 15 cents per pound. It is presently used as a relatively high boiling organic solvent in a number of applications. The compound is very effective in penetrating grease. Its use as an automative degreaser has been suggested and its effectiveness in this respect has been demonstrated by this laboratory. It is very effective as a solvent in other ways such as removing silicones and various types of organic residues from laboratory glassware, cleaning epoxy cement, etc. It may have possibilities as a gel or creme type hand cleaner if it can be shown that trouble from dermatitis is not encountered

The preparation of limonene derivatives has been a subject of study for many years. Since the citrus byproduct limonene is a single optical isomer, one would like to make use of this optical activity, expecially since dipentene, the racemic mixture of d- and l-limonene, is competitive in price with d-limonene and could replace d-limonene for any use not involving optical activity.

The optically active ether derivatives dihydropinol (I), and the ethers (II) and (III), Fig. 1, can be produced from d-limonene in good yield. They should be stable, except under strongly acidic conditions. The use of these ether derivatives as solvents, especially for reactions involving ether complexed intermediates could conceivably result in asymmetric synthesis.

The use of the optically active tertiary Grignard reagent (IV) (Fig. 1) for asymmetric reductions has been reported in the literature. In the particular example concerned, no asymmetric product was produced, however, this negative result is based on the reduction of only a single ketone. Further studies on the use of this asymmetric Grignard reagent with a variety of ketones should be undertaken in order to establish the true nature of its potential as an asymmetric reducing agent.

A recent paper has reported on the use of limonene as a hydrogen donor for the reduction of certain double bonds and nitro groups in the presence of palladium catalyst. p-Cymene is the byproduct. It would be interesting to attempt an asymmetric reduction with this system using d-limonene as the hydrogen donor.

Piperitone and perillartine are related to limonene. Piperitone is used in perfumes and dentifrices to impart a minty flavor and has a current market price of about $5 per pound. Perillartine is a synthetic sweetening agent used commercially in Japan. The use of limonene as a source for the above two compounds was proposed by Dr. Philip Shaw of the Fruit and Vegetable Products Laboratory.

Although the constituents of citrus oils other than limonene only account for 4 to 10% of the total, it might be profitable to utilize some of them commercially, provided that the separation from the oil was reasonably straightforward and assuming that the product is quite active or potent so that its value would be high.

Orange and lemon oil in undiluted form have been recently shown to be potent bacteriostats and fungistats. For example, a concentration of 2000 ppm of orange oil was shown to be as effective in inhibiting bacterial growth in foods as 10 ppm of the antibiotic tylosin. The active ingredient is unknown. The flavonoid compounds nobilentin and tangeretin were shown in a recent article to have fungistatic activity against the fungi responsible for "Mal-Secco" disease of citrus in the Mediterranean area. Fungistatic effects of nobiletin have been verified in another laboratory. The activity of these two compounds as well as other citrus oil components against various microorganisms should be tested, since there seem to be some highly active compounds present. Approximately 6,000 pounds each of nobiletin and tangeratin are available annually from orange and tangerine oil and can be readily separated from these oils.

Valencene is the major sesquiterpene present in orange oil. It can be separated from the oil by a fairly straightforward procedure. The total amount available annually is approximately 2,000 pounds. Valencene can be converted by a one-step reaction to nootkatone, the principal distinctive flavoring component of grapefruit. The related compound, α-vetivone, is one of the major constituents of vetiver oil, which is used in perfumes of an oriental nature. It should be possible to convert nootkatone into α-vetivone by rearrangement of the double bond.

The coumarins bergaptol and umbelliferone can be isolated in fair quantities from certain citrus oils. The related compound, bergaptene, is active as a dermal photosensitizer and molluscacide, while visnadin is a vasodilator used in Europe for treatment of angina pectoris. The conversion of the coumarin raw materials to the active products can be accomplished with reasonably high yields.

CITRUS PULP

The pulp constitutes approximately 45% by weight of the citrus fruit. The flavonoid glycosides hesperedin, naringin and lemon bio-flavonoid complex, containing substantial quantities of eriocitrin and diosmin are produced from the pulp as byproducts of citrus processing (See Figure 2). The estimated amounts available, based on production figures for the 1965-66 season are tabulated below.

Glycoside	Aglycone	Available Amount (lb)
naringin	naringenin	810,000
hesperidin	hesperitin	3,200,000
eriocitrin	eriodictyol	Approximately 100,000

The figures quoted are based on the aglycone. The current price for the glycosides ranges from $5 to $10 per pound.

The glycosides can be broken down to give phloroglucinol plus a substituted phenethylamine. If the stereochemistry at C-2 could be retained, the resultant phenethylamine derivative would be optically active. The current value of phloroglucinol is $10 per pound while the value of the phenyethylamine derivative would vary from $10 to $500 per pound, depending on the particular type of phenethylamine derivative and the stereochemistry of the asymmetric center. Many of the substituted phenethylamines are used as sympathomimetric drugs and in some cases one optical isomer is considerably more active than the other. For example, (-) epinephrine is around twenty times as active as the (+) form and commands a correspondingly higher price. If the flavonoid could be degraded in a fairly straightforward manner so as to give phloroglucinol plus an optically active phenethylamine derivative, the process could represent an economically attractive outlet for flavonoid byproducts.

Although many of these substances are present in minor amounts in citrus, the enzymic reactions leading to their biosynthesis probably can be controlled to increase their normal concentration 100 to 10,000 fold. Temperature, pH, and environmental gas control as well as specific inhibitors can control the metabolic pathways in biological material. Selective use of these agents might make it possible to convert the excised fruit into a miniature fermenter for production of drugs.

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CITRUS WORK AT THE WESLACO LABORATORY

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Approximately two-thirds of the citrus production in Texas is red grapefruit. The major problems associated with processing this variety of fruit are centered around its color and bitterness.

An investigation of the occurrence of naringin in Texas red grapefruit has shown that radioactive $C^{14}O_2$ is fixed in the flavonoids only in the very early stages of fruit growth. Maximum fixation occurred on April 17, when the fruit was 16 mm. diameter and incorporation ceased after May 18, when the fruit was 37 mm. diameter. The total naringin content continued to increase and reached a maximum August 1 approximately 10 weeks after CO_2 fixation ceased to appear in the flavonoids. The study has also shown that fruit set early in the season contained 20 to 25% more naringin during the harvesting season than fruit set 4 months later.

Oil sprays used on Texas red grapefruit for citrus pest control had no significant effect on the color or bitterness of the fruit.

A new variety of red grapefruit ("Hudson") has shown excellent processing characteristics. By late March it was 50% larger than the Ruby Red with 2 1/2 times the lycopene content. The sugar and acid content is approximately the same as other varieties of Texas citrus.

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A REVIEW OF APPLIED RESEARCH ON FRUIT JUICE CRYSTALS

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The preparation of citrus juice crystals has been studied using two different dehydration methods--freeze-drying and foam-mat drying. When orange juice of 10 and 20° Brix was freeze-dried using different sample forms, frozen juice ground into very fine particles appeared to dry best in a large pilot scale freeze-drier. Samples of about 20-mesh U. S. sieve size dried more rapidly and more thoroughly than a slab, and samples of about 60-mesh U. S. sieve size dried even more efficiently. A smaller scale freeze-drier with greater potential for controlling variables has been received and a more carefully controlled experiment is being undertaken at present to verify these findings.

In another study of freeze-dried citrus juices, samples of orange juice were prepared under standard conditions to determine the effects of initial adsorbed gas layer on stability of the product. There has been speculation that, with freeze-dried products, the critical factor for storage might be the nature of the first gas to contact the dehydrated material, i.e., the gas with which the vacuum is broken. Samples of orange juice were prepared where the vacuum was broken with air and these were compared to samples where the vacuum was broken with carbon dioxide. In each of these samples, further variables consisted of the packaging atmospheres--air or carbon dioxide. Storage is in progress.

A series of experiments was conducted to determine what foam-mat drying conditions might need be adapted for changes in characteristics of the concentrate. Several experimental orange concentrates were prepared using varying types of extraction, extraction pressures, and finishing techniques. These resulted in a number of concentrates containing differing amounts of oil, suspended solids, pulp content, and varying in viscosity. These juices were then concentrated and the concentrates were foam-mat dried. No major changes in foam-mat drying conditions were required for the different concentrates. The primary changes required were in foam-making techniques. For concentrates with lesser pulp content and lower viscosities, different foaming agents were required. In these cases, an algin derivative and a high viscosity methylcellulose or carboxy-methylcellulose were required in addition to the regular methylcellulose. There was very little difference in initial quality or storage stability of these experimental samples: all were about the same as standard foam-mat dried crystals.

Flavor evaluations were carried out on orange juice crystals prepared by foam-mat drying, used with different levels of "locked-in" oil in cooperation with the Statistical Reporting Service, U. S. Department of Agriculture, Washington, D. C. Untrained tasters preferred samples with increasing oil content up to .030% (g. oil/100 ml juice). From .030% to .060% there was no significant difference in preference. With grapefruit juice, increasing levels of oil were preferred from .005% to .012%. Based on these studies samples of orange and grapefruit crystals with higher oil content were prepared.

Storage life of these samples was extended considerably over that found in previous studies. In another series of experiments cold-pressed peel oil was added to the concentrate prior to drying and the amount retained in the dried product was determined by the bromate titration method. Approximately 60% added oil was retained. There was little difference between the quality of these samples and conventional samples containing "locked-in" oil. The amount of oil retained after drying varied from 55 to 75% depending upon the original level of oil and the drying conditions.

Sulfur dioxide was added in the form of sodium bisulfite to orange concentrate prior to drying. The amount of SO_2 was then determined in the final product on a basis of ppm in reconstituted juice. Amounts varying from about 20 ppm to about 200 ppm SO_2 were used. There was some extension of storage time before a detectable difference occurred when higher levels of SO_2 were used. Levels of SO_2 from about 20 to about 100 ppm had little effect.

Foam-mat drying has been extended to a number of subtropical and tropical fruits including guava, pineapple, and strawberry. Foaming conditions have been developed and drying conditions have been studied. For these fruits, usually additional thickening agents such as high viscosity methylcellulose or algin derivatives were required. Products with good initial quality have been prepared and storage stability of these is presently under study. These products have been blended with foam-mat dried orange and grapefruit juices to provide additional new fruit-drink products as well.

PRINCIPLES OF MICROFLAKE FOOD DEHYDRATION

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The Microflake Food Dehydration System (MFD) was designed to fill a gap in the spectrum of existing drying methods. It is an atmospheric, continuous belt-drying process for liquid food foams. In the latter respect, i.e., food foams, it is akin to the USDA foam-mat process.

The dehydration is accomplished in approximately 60 seconds at a maximum product temperature of 170°F. This is accomplished by casting food foam in a layer of approximately 10 mills to 40 mills on a solid stainless steel belt, and heating from below by the direct condensation of steam, and from above by heated air. The product is doctored from the belt in the form of small, porous crystals.

The unique features of the MFD process reside in the engineering advances in the steambox dryer design, heated air system, foam generation, and precision in film casting, which makes the "low temperature, short-time" drying cycle possible at overall evaporation rates of 1 pound to 3 pounds of water removed per square foot of dryer surface per hour.

In addition, since the air chambers and steam boxes are divided into separate zones, the product temperature along the belt is precisely controlled. Further control of product temperature in the doctoring zone is used to modify the physical characteristics of the doctored product.

A REVIEW OF CONSUMER RESEARCH ON CITRUS PRODUCTS

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About a year and a half ago, we began planning a household placement test for foam-mat dried grapefruit juice crystals from the Fruit and Vegetable Products Laboratory* in Winter Haven, Florida in cooperation with Agricultural Research Service and the Florida Citrus Commission.

The overall objective of the research was two-fold: To evaluate consumer acceptance of foam-mat dried Grapefruit juice crystals and to provide insights into the measures which might be taken to effectively market citrus crystals of any flavor.

The resulting study has been conducted under contract with a private research firm. It was undertaken with the financial support of the Florida Citrus Commission and ARS. The Florida Citrus Commission also obtained cooperation from the Riegel Paper Corporation of New York City for the packaging of the crystals, which were put in preformed yellow and green pouches in laminated paper-foil-polyethyline material. Each pouch contained enough crystals to reconstitute into a little over a pint of juice by adding 16 ounces of water. The sweetened crystals had a Brix acid ratio of 13.5, the unsweetened 9.5.

Respondents were selected from a probability sample of households in the Standard Metropolitan Statistical Area (SMSA) of Pittsburgh, Pennsylvania. The sample was designed to yield about 400 product placements--200 among homemakers who said grapefruit juice had been used in their homes at least once during the preceding 6 months and 200 who said it had not. The first interview with the homemaker was to obtain her opinions about grapefruit juice in general and her reaction to the concept of crystals. Each respondent was then given a supply of either sweetened or unsweetened grapefruit juice crystals, and asked to serve the juice to each household member 12 years of age or older. About a week later, the interviewer returned to obtain information about the homemaker's reactions to the crystals and leave sweetened crystals where unsweetened had already been tested and vice versa. The interviewer later obtained opinions about the second package of crystals. Both times all of the household members 12 years of age and over were asked to fill out cards on which they indicated their comments and rated the crystals and grapefruit juice in general on a 9-point hedonic scale.

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* Southern Utilization Research and Development Division, Agricultural Research Service

The interviewing was in May and June 1967. The initial interview was completed with approximately 450 homemakers. Cooperation in testing both types of crystals was maintained with 374 households.

Approximately 4 households in 10 reported that grapefruit juice had been used in the preceding six months, and about two-thirds of the users indicated grapefruit juice was served in their households at least once a week on the average.

All users were asked about the advantages and disadvantages of canned and frozen concentrated grapefruit juice. Among these homemakers, 6 in 10 said that ease of preparation or serving is the main advantage of the canned form.

While taste or flavor was considered an advantage by only 1 in 10 for the canned form, about 4 in 10 mentioned taste or flavor when discussing advantages of the frozen concentrated form.

Better than half the respondents indicated they had used a powder or crystal form of drink. Those homemakers who had used any kind of powder or crystal were asked their opinions about the advantages and disadvantages of such products. They were considered easy, fast, and quick to prepare, a task the children could do. The fact that as much or little as needed could be made at one time was also considered an advantage, and ease of storage was mentioned frequently. Those who had used this type of product were just about as likely to be critical of the taste or flavor as they were to consider it an advantage: Approximately 1 in 4 spoke favorably of the taste or flavor, while 1 in 4 made negative comments about it.

Before respondents were informed that we would like to have them try a new juice product, grapefruit juice crystals were described. Respondents were then asked "How likely would you be to try this kind of product." Almost 40 percent of the users said they would <u>definitely</u> like to try it, and the same proportion said that they would <u>probably</u> be interested in trying it. Approximately half of the nonuser homemakers also indicated interest in trying grapefruit juice crystals.

Many of the advantages and disadvantages homemakers ascribed to the idea of the crystals were similar to the reactions to powdered drinks on the market.

Relatively few (less than 1 in 5) mentioned taste or flavor as presumed advantages, and about 1 in 5 assumed that the taste or flavor of a crystal product would not be as good as other forms of grapefruit juice.

The ratings given by household members after tasting the crystals tended to parallel the results from the sensory evaluation laboratory, with crystals scoring lower than regular grapefruit juice. The sweetened crystals seemed to be liked a little better than the unsweetened version by individuals who did not usually drink grapefruit juice; there was no appreciable difference in the ratings of the sweetened and unsweetened versions among grapefruit juice drinkers.

In response to a question on what they particularly liked about the crystals, approximately 3 household members in 10 commented favorably on the taste or flavor, but better than 4 in 10 indicated that there was nothing they especially liked. And in response to a question on dislikes, roughly half were critical of the taste or flavor. Only one-third said that there was nothing they disliked about the crystals.

When only the homemaker was considered, the pattern of ratings was essentially the same, with crystals scoring below other forms of grapefruit juice and with the sweetened form of crystals outscoring the unsweetened form. The advantages and disadvantages cited by the homemakers were also quite similar to what all household members said they especially liked or disliked. But roughly half the homemakers volunteered favorable comments about preparation or serving, saying the crystals were convenient and easy to use, or that they mixed well. Less than 1 homemaker in 10 mentioned any difficulty in getting the crystals to dissolve well or quickly. When asked specifically about whether the crystals were easy or hard to mix, one-third of the homemakers indicated the crystals presented some difficulties, and in a comparison of the grapefruit juice usually used with the crystals on ease of preparation, about one-half chose their regular grapefruit juice, one-third thought the crystals were easier, and the remainder (16 percent) had no preference.

The homemakers were asked how likely they would be to buy the grapefruit juice crystals if they were available in local stores and what they would be willing to pay. Answers to questions such as this cannot be taken literally as predictors of future purchases. However, they do indicate interest in a product.

Just about half of the users and one-third of the nonusers of grapefruit juice indicated they definitely or probably would purchase crystals if they were available. About 1 in 4 said they would definitely <u>not</u> buy them, and the remainder were divided among those who were undecided or thought they probably wouldn't purchase the crystals.

When asked the highest price she would be willing to pay for enough grapefruit juice crystals to reconstitute into a quart of juice, if grapefruit juice in general were selling for 32 cents a quart, almost half the respondents thought they would pay as much or more for the crystals as for regular grapefruit juice.

Among the grapefruit juice users who said they would consider purchasing the crystals, the majority indicated they thought more than half of their purchases of grapefruit juice would probably be of the crystals rather than the form they were currently using.

When asked about possible improvements, roughly 6 in 10 suggested improving the taste or flavor. The only other suggestion made by as many as 15 percent was concerned with making the product easier to mix or making it dissolve more readily.

The data revealed that even among those homemakers who thought they would be interested in buying crystals, a large proportion were somewhat critical of the flavor. The product characteristics which appealed to them seemed to be the several conveniences offered by this form: Non-refrigerated storage, space-saving, and being able to mix the desired quantity for a serving.

All-in-all, then, the results among a sample of homemakers in Pittsburgh, Pa. suggest that the concept of crystals was generally well received, but that there are still some product problems. Improving the flavor, for example, would probably enhance the chances of successfully marketing the crystals. The fact that the sweetened crystals faired somewhat better in the ratings suggests one possible direction of efforts at flavor improvement. And developing a product that would dissolve more easily would probably also help to increase its popularity, although to a lesser extent.

9-7-67

Flavor Extraction with Liquid CO_2

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Western Utilization Research and Development Division
Albany, California

Flavor components of citrus products can be extracted at room temperature by direct contact with liquid carbon dioxide. The extraction must be carried out in apressurized system (700-800 lb/in^2), for liquid CO_2 cannot exist at lower pressures at ambient temperatures. Liquid carbon dioxide is a good solvent for many of the higher molecular weight flavor constituents of juices and has the added advantage that it is non-toxic and is easily separated from both the extract and raffinate by reducing the system pressure to one atmosphere. The CO_2 vaporizes rapidly with little residual dissolved in the liquid.

There are several other vapors with critical points around room temperature. Some of these could possibly be employed for extraction as liquified vapor under high pressure, but carbon dioxide was chosen for several characteristics. It is desirable for its selectivity, nontoxicity, and safety.

A versatile, continuous extraction system has been setup in our laboratory. The equipment was designed for a 1000 psi working pressure and can operate with either cocurrent or countercurrent circulation. The CO_2 circulating system is equipped with stripping and condensing columns to vaporize and recondense the

carbon dioxide, leaving the extracted flavor components and dissolved water behind as an extract, or "essence". Very little of the extracted flavor is vaporized with the CO_2, for the temperature variations are quite small. The extraction is carried out at 25° C, while the vaporization is at 28° C and the condensation is at 22° C. The critical temperature of CO_2 is 31° C.

Liquid CO_2 is a nonpolar liquid which is especially useful in extracting other nonpolar compounds such as hydrocarbons. Higher molecular weight polar compounds are also easily extracted. Alcohols, ketones, esters, and aldehydes may be almost completely extracted if they contain five or more carbon atoms. The highly polar, low molecular weight compounds, such as ethyl alcohol, could probably never be extracted to any extent. Sugars and acids exhibit very little solubility in liquid CO_2 and are virtually not extracted.

To point out the increasing selectivity of CO_2 for molecules of increasing molecular weight in a homologous series, distribution coefficients, between liquid CO_2 and water, of members of the aliphatic alcohol series are shown. The distribution coefficient gives the rates of concentration, at equilibrium, of a compound in the CO_2 phase to the same compound in the aqueous phase.

Alcohol	Distribution Coefficient
n-propanol	0.34
n-butanol	3.1
n-pentanol	12
i-pentanol	10.5
n-hexanol	37
n-heptanol	125

The list of distribution coefficients indicates that the C_5 compounds can be easily extracted, while the C_4 compounds are marginal. The distribution coefficient for d-limonene, a major constituent of orange peel, is about 55, showing that it can be almost completely extracted. Liquid CO_2 extracts some color from orange juice, for the CO_2 becomes yellow during extraction. The extent of color extraction has not been determined.

The extraction of juices could be cycled until the extract was as concentrated as desired if it were not for the dissolved water carried by the CO_2 phase. This solubility, though small, limits the extraction. Water is soluble in liquid CO_2 to the extent of about 1% by weight, and this water remains in the extract when the CO_2 is evaporated. The concentration of the aroma is limited by this water carry-over. However, aromas of the magnitude of 150,000-fold have been achieved with some products, although not yet with orange.

9-6-67

Juice Concentration by Reverse Osmosis

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Western Utilization Research and Development Division
Albany, California

Orange juice can be concentrated without adding heat or losing orange solids by a membrane process called reverse osmosis. Furthermore, most of the orange aroma is retained.

In reverse osmosis water diffuses under pressure through a semipermeable membrane. The success of the process for juice concentration depends upon the selectivity of the membrane and upon the rate of water removal. Selectivity is the ability of the membrane to pass water but retain dissolved solutes and suspended solids; it is determined by the chemical composition of the juice and of the membrane. For the cellulose acetate membranes now in use, fruit sugars and acids are well retained even at relatively high water permeation rates. In general, the aroma compounds of fruit juices are more difficult to retain but orange aroma is an exception. The oil soluble constituents of orange aroma do not permeate the membrane and are completely retained. Chromatographic analysis shows that a fraction of the small, water-soluble esters, aldehydes, and alcohols are lost through the membrane, particularly at high water removal rates. In spite of this, a concentrate prepared by reverse osmosis retains at least three times as much of the water-soluble aroma as does a concentrate made with cut-back juice and thus retains an excellent fresh orange flavor.

The permeation rate is not independent of selectivity, but depends on how the membrane is made. Tight membranes, which retain the water-soluble volatiles best, have low water removal rates, resulting in a longer product residence time and a more expensive process. Membranes made with higher permeation rates require less membrane surface, or lower pressures, and hence lower equipment costs, but can result in the loss of some volatiles or even dissolved solids. Sugar solutions of low osmotic pressure can be concentrated with excellent sugar retention at rates up to 30 gallons per square foot per day. As the osmotic pressure of the feed increases the permeation rate decreases according to the formula

$$\text{Permeation rate} = KA(P - \Delta\pi)$$

where P is the hydrostatic pressure applied to the feed, $\Delta\pi$ is (approximately) the osmotic pressure of the feed, A is the membrane surface area, and K is a permeation coefficient characteristic of the membrane. The osmotic pressure of a four-fold orange juice concentrate is about 1300 psi. Pressures necessary to produce practical permeation rates are therefore at least 1500 psi or higher. Suspended solids do not seriously interfere with reverse osmosis concentration.

There is no evidence at present that membrane life is a limiting factor in juice concentration by reverse osmosis. Periodic cleaning of the membrane equipment will be necessary, of course, and since

cellulose acetate membranes are inexpensive, replacement of membranes in the dismantled equipment should not be costly.

A device has been designed - WURSTACK - which combines high strength with sanitary construction. This unit contains a high proportion of membrane surface to juice holdup - thus keeping residence time of the concentrate low. This design is presented and is recommended for R & D use at least.

UNITED STATES DEPARTMENT OF AGRICULTURE

AGRICULTURAL RESEARCH SERVICE

LIST OF CITRUS PUBLICATIONS

AND PATENTS

(September 1, 1966 - August 31, 1967)

Reprints of publications may be obtained without cost by addressing request to the Laboratory listed.

Patents may be obtained only by purchase from the U. S. Patent Office, Washington, D. C. 20250, for 50 cents each.

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SOUTHERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

FRUIT AND VEGETABLE PRODUCTS LABORATORY
600 Avenue S, N. W.
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Held at Winter Haven, Florida,. October 5, 1966.

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WESTERN REGIONAL RESEARCH LABORATORY
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Albany, California

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WESTERN UTILIZATION RESEARCH AND DEVELOPMENT DIVISION

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1967 CONFERENCE ON CITRUS CHEMISTRY AND UTILIZATION

October 13, 1967
LANDMARK MOTOR LODGE
Winter Haven, Florida

Southern Utilization Research and Development Division
Agricultural Research Service
United States Department of Agriculture
New Orleans, Louisiana

FOREWORD

This Conference is sponsored annually by the Southern Utilizataion Research and Development Division of the Agricultural Research Service, USDA. Its purpose is to report research developments in the area of citrus processing and utilization and to provide for an exchange of information that will benefit the industry and future research.

Those interested are cordially invited to attend and participate in the discussions. Dr. M. K. Veldhuis, Chief, U. S. Fruit and Vegetable Products Laboratory, 600 Avenue S, N. W., Winter Haven, Florida, will be pleased to make your hotel reservation. No registration fee will be required.

C. H. Fisher

C. H. Fisher, Director

Southern Utilization Research and Development Division
Agricultural Research Service
U. S. Department of Agriculture

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PROGRAM

Landmark Motor Lodge
Winter Haven, Florida

Friday, October 13, 1967

8:00 A. M. Registration

9:00 A. M. CALL TO ORDER

Vernon C. Praschan
Fruit and Vegetable Products Laboratory
National Dairy Products Corporation
Glenview, Illinois

OPENING REMARKS

C. H. Fisher, Director
Southern Utilization Research
and Development Division
New Orleans, Louisiana

Presiding: **H. E. (Bert) Schulz,** Florida Chemical Company, Inc., Lake Alfred, Florida

ANALYSES OF STORED FOAM-MAT ORANGE AND GRAPEFRUIT CRYSTALS AND OF MODEL SYSTEMS

Philip E. Shaw, James H. Tatum, and Robert E. Berry
U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Florida

When foam-mat dried orange and grapefruit crystals were stored under identical conditions, orange was first to develop a detectable flavor change. At that point both orange and grapefruit have been analyzed. Results of these studies indicated that for both samples the same products are formed during storage in about the same quantities. In other studies to aid in identifying some compounds formed in orange and grapefruit crystals during storage, fructose-base and ascorbic acid model systems were investigated. The findings complemented those of an earlier study and suggested possible precursors for some of the storage products. Also, further efforts have been made to correlate ultraviolet absorption with storage and heat decomposition in orange crystals and chilled juice. For a given sample of chilled juice, correlation was noted between heat treatment and ultraviolet absorption. However, this correlation was not applicable between different samples of chilled juice or to orange or grapefruit crystals.

A PROCEDURE FOR OBTAINING RADIOACTIVE NARINGIN FROM GRAPEFRUIT LEAVES FED L-PHENYLALANINE-^{14}C

James F. Fisher
U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Florida
(To be presented by **M. K. Veldhuis)**

Radioactive naringin, naringenin-7β-neohesperidoside, the principal bitter constituent of grapefruit and its radioactive tasteless isomer, naringenin-7β-rutinoside were isolated from young grapefruit leaves fed L-phenylalanine-^{14}C. The method employs radiolabeled L-phenylalanine which is taken up by young grapefruit leaves through the petioles. The leaves are then allowed to metabolize the phenylalanine during periods of 12 hours of light and 12 hours of dark. Extraction of the leaves with hot methyl alcohol, followed by concentration and column chromatography afforded both the bitter naringin and its tasteless isomer. Final separation and purification of both compounds were accomplished by thin-layer chromatography. The availability of these radiolabeled compounds will enable us to advance our knowledge concerning the site of synthesis and translocation of naringin as well as its biosynthesis and metabolism in the grapefruit plant. It has now been demonstrated that L-phenylalanine is a precursor to naringin in grapefruit leaves.

BASIC STUDIES ON ENZYMES IN CITRUS PRODUCTS

Joseph H. Bruemmer, Robert A. Baker, and Bongwoo Roe
U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Florida

A program has been initiated on the enzymes in citrus products with a view toward improving the flavor and flavor stability of citrus juices. If citrus products contain the enzymes that synthesize the important flavor components of citrus juice, then a method of utilizing this potential for flavor enhancement might be developed.

As the first step in assessing this enzyme potential of citrus, the distribution of pyridine nucleotide coenzymes was examined. The reduced form of one of the coenzymes, nicotinamide adenine dinucleotide phosphate (NADP) is a key reactant in the biosynthetic pathways of the oxygenated terpenoids and aliphatic compounds that have been identified with citrus flavor.

We have found a relatively high concentration of reduced NADP in juice vesicles from mature oranges and

grapefruit. In this regard, at least, citrus juice has the capability of synthesizing the flavor compounds found in essence.

Citrus juice was shown also to have oxidase activities for ascorbic acid, various polyhydric compounds, and various natural and artificial oxidation-reduction indicating compounds. These oxidase activities can be coupled to the oxidation of the pyridine nucleotide coenzymes through other enzymes found in citrus juice.

CHEMICAL CHARACTERIZATION OF LEMON JUICE PRODUCTS

Carl E. Vandercook
Fruit and Vegetable Chemistry Laboratory
Western Utilization Research and Development Division
Pasadena, California

An increasing percentage of the U. S. lemon crop is being processed into juice and juice products. The effect of processing on the constituents must be determined to guide processing improvements. Constituents investigated included total and individual amino acids, l-malic acid, total and individual phenolics, sterols, and carotenoids. The amino acid, malic acid, and phenolics data have been treated by a multiple regression analysis approach to give an equation which can predict the citric acid content of a sample. Differences between measured and predited citric acid values were relatively small in all samples tested. The influence of processing techniques, fruit variety, season, growing area, storage conditions, and chemical preservatives on the composition of juice samples and the application of the multiple regression approach will be discussed.

WHAT IS A NATURAL FLAVOR?

Samuel R. Hoover, Assistant Deputy Administrator
Nutrition, Consumer and Industrial Use Research
Agricultural Research Service
U. S. Department of Agriculture
Washington, D. C.

Flavors come in various types and sizes. A few occur just as we savor them; citrus fruits are of this type. Others are produced enzymically when tissue is damaged, onions and garlic are the classical examples. Some are produced by fermentation. Processing steps produce flavors, ham and corned beef illustrate these. Most of our foods derive their essential flavor from chemical reactions that occur during

cooking. We have herbs and seasonings, monosodium glutamate and now nucleotides. Which of these are natural flavors?

POTENTIAL UTILIZATION OF SOME CHEMICALS FROM CITRUS FRUIT

Eric D. Lund
U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Florida

A number of potential new chemical byproducts from citrus have been proposed recently by members of the staff of the Fruit and Vegetable Products Laboratory. The value of these products has been estimated in terms of availability of raw materials and potential economic return from the product.

Raw materials concerned include flavonoids and coumarins from citrus pulp and limonene, valencene, nootkatone, and other terpenoids from peel oil. Proposed uses for the products encompass bacteriostats, fungistats, pharmaceuticals, degreasers, perfumery components, flavoring materials, synthetic sweeteners, and solvents for the production of optically active compounds.

12:00 Noon Luncheon

1:30 P. M.

Presiding: **C. Reed Sutherland,** Birdseye Division, General Foods Corporation, Winter Haven, Florida

CITRUS WORK AT THE WESLACO LABORATORY

Bruce J. Lime, Roger F. Albach, and Filmore I. Meredith
Food Crops Utilization Research Laboratory
Weslaco, Texas

When grapefruit sets fruit at different times of the year, that fruit which is set earliest contains the greater amount of naringin; while the other flavanones show little differences. Fruit set in either December or April reach a peak naringin content in July; after maturing an additional year, naringin content shows another peak in June.

Use of oil sprays on trees during the fruit growing period had no apparent effect on naringin or carotenoid content of the fruit.

The carotene pigments in the "Hudson" grapefruit, a seedy, redfleshed fruit, were analyzed through the season. Lycopene content reached a maximum and then started a slow decline. The mg/fruit lycopene in the "Hudson" was approximately 3 times higher than in the Redblush by the end of the experiment.

Sections have been prepared from the Duncan, Redblush, and "Hudson" variety of grapefruit. The sections from the "Hudson" compare with the Duncan in firmness.

A REVIEW OF APPLIED RESEARCH ON FRUIT JUICE CRYSTALS

Robert E. Berry, Owen W. Bissett, Charles J. Wagner, Jr., and James L. Froscher
U. S. Fruit and Vegetable Products Laboratory
Winter Haven, Florida

Freeze-drying studies were made on the relationship between sample form and rate of drying. Samples in small pieces dried more easily than larger pieces. In another study the vacuum was broken and the samples were stored in air or carbon dioxide. These were evaluated for storage stability. Although incomplete, a progress report will be made. Crystals were prepared by foam-mat drying orange concentrates varying greatly in physical characteristics. Stability was the same regardless of physical characteristics of the concentrate. With some concentrates carboxyl-methyl cellulose or algin were required to obtain sufficient viscosity for foam-making. Flavor evaluations were carried out on orange crystals with different levels of: (1) locked-in oil; (2) oil in concentrate prior to drying; (3) SO_2; (4) other flavoring or stabilizing materials. Untrained tasters preferred higher levels of oil than had been previously used. When oil was added to concentrate, 55% to 75% was retained after drying. The addition of SO_2 enhanced storage stability of orange crystals. Foam-mat dried samples of guava, pineapple, and strawberry have been prepared.

PRINCIPLES OF MICROFLAKE FOOD DEHYDRATION

Raymond J. Moshy
Research Division
American Machine and Foundry Company
Springdale, Connecticut

The Microflake Food Dehydration System (MFD) was designed to fill a gap in the spectrum of existing drying

methods. It is an atmospheric, continuous belt-drying process for liquid food foams. In the latter respect, i.e., food foams, it is akin to the USDA foam-mat process.

The dehydration is accomplished in approximately 60 seconds at a maximum product temperature of 170° F. This is accomplished by casting food foam in a layer of approximately 10 mills to 40 mills on a solid stainless steel belt, and heating from below by the direct condensation of steam, and from above by heated air. The product is doctored from the belt in the form of small, porous crystals.

The unique features of the MFD process reside in the engineering advances in the steambox dryer design, heated air system, foam generation, and precision in film casting, which makes the "low temperature, short-time" drying cycle possible at overall evaporation rates of 1 pound to 3 pounds of water removed per square foot of dryer surface per hour.

In addition, since the air chambers and steam boxes are divided into separate zones, the product temperature along the belt is precisely controlled. Further control of product temperature in the doctoring zone is used to modify the physical characteristics of the doctored product.

The basic engineering principles and economics of this process will be discussed, as well as product characteristics —with emphasis on citrus products.

A REVIEW OF CONSUMER RESEARCH IN CITRUS PRODUCTS CONDUCTED BY SRS

Margaret Weidenhamer, Chief
Special Surveys Branch
Standards and Research Division
Statistical Reporting Service
Washington, D. C.

Progress to date on a study to evaluate consumer acceptance of the Winter Haven Laboratory's foam-mat dried grapefruit juice crystals will be discussed. Data were collected early this summer from respondents in a probability sample of households in Pittsburgh, Pennsylvania. Household members evaluated both sweetened and unsweetened crystals.

Several sensory evaluation laboratory tests on citrus juices will also be reported. These tests were conducted with an untrained panel of USDA employees on their reactions to variations in Brix/acid ratios, percent of peel oil, and amounts and types of sweeteners added.

FLAVOR EXTRACTION WITH LIQUID CO_2

John M. Randall and **Arthur I. Morgan, Jr.**
Engineering and Development Laboratory
Western Utilization Research and Development Division
Albany, California

Liquid carbon dioxide can be brought into direct contact with citrus products at 900 pounds per square inch pressure and room temperature to extract flavor components. After pressure reduction, the carbon dioxide evaporates, leaving behind the extracted flavor substances. Carbon dioxide remaining in the citrus product raffinate is not objectionable. As a solvent, liquid CO_2 acts very much like a non-polar liquid. It extracts hydrocarbons, especially those with a long hydrophobic chain. It removes most of the flavor components, especially aldehydes and ketones, quite well. It absorbs about 1% water. It does not dissolve carotenoid pigments very well. An apparatus has been built to study the counter-current liquid-liquid extraction under the conditions required. Partition coefficients and limited phase data are presented. An experimental scheme for carrying the process out is proposed.

JUICE CONCENTRATION BY REVERSE OSMOSIS

R. Larry Merson and **Arthur I. Morgan, Jr.**
Engineering and Development Laboratory
Western Utilization Research and Development Division
Albany, California

Reverse osmosis can remove water from citrus juice without heat and without much removal of volatile components, when a modified cellulose acetate membrane is used. Juice hydrostatic pressures as high as 1500 pounds per square inch are required to make commercial orange juice concentrate, if one-stage operation is used. Permeation rates under these conditions are low, probably not more than 1 gallon of water per day per square foot of membrane. Some nonvolatile acids and some small alcohols permeate the membrane to a small extent, together with the water. Very highly aromatic orange juice concentrates have been made by this method. A sanitary low-holdup device called the WURSTACK has been designed to carry out the experimental studies on reverse osmosis. Routine casting of the cellulose acetate membrane is described.

ADJOURNMENT

There will be a meeting of the IFT on the night of October 12 in Winter Haven at which the guest speaker will be Dr. Samuel R. Hoover, Assistant Deputy Administrator, Nutrition, Consumer and Industrial Use Research, Agricultural Research Service, USDA. Dr. Hoover will speak on "Synthetic Foods—Question Mark." "A Review of Present and Future Competetive Situation of Farm Products for Supplying Our Food Needs vs. Chemical and Biochemical Synthesis." The Social Hour will be at 6:30 P.M.; Dinner at 7:30 P.M.; and the Program will begin at 8:30 P.M. at the Cypress Gardens Sheraton.

Your attention is called to the following meeting:

18th Annual Citrus Processors' Meeting
University of Florida Citrus Experiment Station
Lake Alfred, Florida (Zip Code 33850)
Thursday, October 12, 1967

Registration will begin at 9:30 A.M.

The Stataion is only a few miles from our Laboratory. Further details of this meeting may be obtained from Dr. F. W. Wenzel at the above address.